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Isotope compositions (C, O, Sr, Nd) of vertebrate fossils from the Middle Eocene oil shale of Messel, Germany: Implications for their taphonomy and palaeoenvironment

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ABSTRACT

The Middle Eocene oil shale deposits of Messel are famous for their exceptionally well-preserved, articulated 47-Myr-old vertebrate fossils that often still display soft tissue preservation. The isotopic compositions (O, C, Sr, Nd) were analysed from skeletal remains of Messel's terrestrial and aquatic vertebrates to determine the condition of geochemical preservation. Authigenic phosphate minerals and siderite were also analysed to characterise the isotope compositions of diagenetic phases. In Messel, diagenetic end member values of the volcanically-influenced and (due to methanogenesis) ^{12}C-depleted anoxic bottom water of the meromictic Eocene maar lake are isotopically very distinct from in vivo bioapatite values of terrestrial vertebrates. This unique taphonomic setting allows the assessment of the geochemical preservation of the vertebrate fossils. A combined multi-isotope approach demonstrates that enamel of fossil vertebrates from Messel is geochemically exceptionally well-preserved and still contains near-in vivo C, O, Sr and possibly even Nd isotope compositions while bone and dentine are diagenetically altered.

Enamel of the hippomorph perissodactyl *Propalaeotherium* has low δ^{13}C values (-9 ± 0.7‰), typical for C_3-plant-feeders. Dentine of the same teeth has δ^{13}C values 15–17‰ higher, amongst the highest $\delta^{13}C_{bioapatite}$ values reported for terrestrial vertebrates. This reflects diagenetic carbonate exchange with the strongly ^{12}C-depleted anoxic lake bottom water. Enamel $^{87}Sr/^{86}Sr$ values (~0.711 ± 0.001) are consistent with *Propalaeotherium* feeding on Palaeozoic bedrocks surrounding Lake Messel and suggests that the basaltic tuff ring around the maar was already eroded 640 ka after its formation. Dentine has, however, much lower, volcanically influenced $^{87}Sr/^{86}Sr$ (~0.706) due to diagenetic Sr uptake from the lake water/oil shale. Enamel $\delta^{18}O_p$ values (~18 ± 0.6‰) of *Propalaeotherium* are 2–3‰ lower than those of bones and scales of aquatic vertebrates that lived in the ^{18}O-enriched lake water. Using transfer functions, a $\delta^{18}O_{H_2O}$ value of -5 ± 1‰ for meteoric water and a MAT of ~18 ± 2.5 °C were reconstructed for Messel.

1. Introduction

Messel near Darmstadt in Germany, is a world-famous conservation-Lagerstätte (UNESCO-World Heritage Site) which is renowned for the articulated vertebrate fossils from the middle Eocene lacustrine oil shale deposits, which often have exceptional preservation of soft tissues such as fur, feathers and gut contents (e.g., Schaal and Ziegler, 1992; von Koenigswald et al., 1998; Franzen, 2007; Gruber and Micklich, 2007; Vinter et al., 2010). These vertebrate fossils represent an important window into the evolution of early mammals and other vertebrate taxa, and their palaeobiogeographic distribution and palaeobiology and have thus been extensively studied by palaeontologists over the last 140 years. However, geochemical investigations of these exceptionally well-preserved vertebrate fossils are scarce (Schweizer et al., 2007; Gehler et al., 2011; Herwartz et al., 2013a, b; Pack et al., 2013). Soft tissue remains from aquatic and terrestrial vertebrates are still well-preserved and their carbon and nitrogen isotope compositions were analysed to infer trophic relationships in the Eocene Messel food web (Schweizer et al., 2007). The diagenetic alteration of the oxygen isotope composition in the PO_4-group of bioapatite from a rodent tooth was assessed using triple oxygen (^{16}O, ^{17}O, ^{18}O) isotope analysis. The presence of a negative Δ^{17}O anomaly in enamel (derived from in vivo inhaled isotopically anomalous air oxygen) demonstrated the preservation of original $\delta^{18}O_p$ values in enamel (Gehler et al., 2011). This Δ^{17}O anomaly was then used as a proxy to reconstruct the Eocene atmospheric pCO_2 at Messel to 740 ± 430 ppmv, assuming a similar gross primary production as today (Pack et al., 2013). Radiometric Lu–Hf dating of various Messel vertebrate fossils, authigenic siderite and

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